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A SAXS Characterization of Particle Aggregation in TiO_2 Sol-Gel System

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The gelation process of homogeneous titanium iso-propoxide solutions was studied as a function of reaction time by small-angle X-ray scattering (SAXS). The scattered intensities at the final stage of the gelation are characteristic of a particle aggregation. The SAXS measurement shows that primary particles are formed just after the gelation process starts and aggregate to form fractal structures in the titanium iso-propoxide solutions. The radii of gyration of the primary particles vary as a function of molar ratio R ($=H_2O/Ti$), 5.0 Å for $R=1$, 12.0 Å for $R=2$ and 11.0 Å for $R=3$ and almost hold constant throughout the gelation process. These primary particles aggregate to form fractal structures, whose fractal dimensions d_f are 1.62 for $R=1$, 1.74 for $R=2$ and 2.51 for $R=3$.

KEY WORDS: SAXS/ Sol-Gel/ Fractal Structure/ Aggregation/ TiO_2

1. INTRODUCTION

Titanium oxide glass is known to be a useful material for industrial applications and its peparation is well suited to sol-gel method. The structural evolution of titanium alkoxide in solution under variuos chemical conditions is one of the most important controling factors for TiO_2 glass formation by sol-gel process. Kallala *et al.*[1] studied the effect of chemical conditions, especially of molar ratio H^+/Ti, on the preparation of the sol, transparent gel, turbid gels and precipitates of titanium alkoxide by the sol-gel method. They evaluated the fractal dimension of various phases appearing in the sol-gel process of titanium alkoxide by small-angle X-ray scattering.

In the sol-gel process of silicon alkoxides, Iler showed that the silicic acid polymerizes into discrete particles at the initial stage of the reaction and later the particles aggregate into chains and networks.[2,3] Himmel *et al.*[4] showed by small-angle X-ray scattering measurements that elementary particles SiO_2 of 5～10 Å in diameter are formed at the beginning of the process and these particles agglomerate to form fractal secondary clusters in the sol-gel process under the acid-catalyzed condition. Zarzycki[5] showed by the electron microscopic observation of dense SiO_2 gels that the gel texture is a compact assemblage of spherical particles, nearly monodirpersed and he suggested a hierarchical type of aggregation.

The small-angle X-ray scattering (SAXS) techniqhue has an adequate resolution to observe inhomogeneities in the range $10～10^3$ Å and can provide information about the hierarchical type

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of aggregation in the sol structure. The measurement must be done in the wide scattering vector range.

The hydrolysis rate of titanium alkoxide is very fast and the colloidal particles precipitate easily. We made a SAXS study of the aggregation process of titanium iso-propoxide solution of molar ratio $Ti : EtOH : H_2O : HCl = 1 : 2 : 2 : 0.36$. prepared at various water-supply rates.[6] Slow water-supply rate keeps the solution transparent throughout the gelation and provides a fractal structure of about 120 Å in size. On the other hand, the solution of fast water-supply rate becomes opaque before the gelation point and has a not well-defined fractal structure. Its correlation length is very small, about 20 Å. In this paper we report the result of the SAXS study on the sol-gel process of homogeneous titanium iso-propoxide solutions.

2. EXPERIMENTAL

Titanium tetra-iso-propoxide ($Ti(O\text{-}iPr)_4$, Wako Chemical Co., Ltd.) was mixed with a half of the prescribed amount of distilled ethyl alcohol (EtOH). After being stirred for 30 minutes in a dried nitrogen atmosphere, the $Ti(O\text{-}iPr)_4$ solution was mixed with the prescribed amounts of aqueous solution of HCl and EtOH. The starting solutions of molar ratio $Ti(O\text{-}iPr)_4 : EtOH : water = 1 : 2 : R : 0.18 \times R$ with $R=1$, 2 and 3 were prepared for SAXS measurements. The aqueous solutions were supplied at the constant rates 0.041 R/min for $R=1$, 0.065 R/min for $R=2$ and 0.011 R/min for $R=3$ mixtures into one mol $Ti(O\text{-}iPr)_4$ through an injector joined onto a micrometer-head driven by a speed-cntrollable motor. All the preparations were made at room temperature. The pH's of the prepared solutions were 3.3 for $R=1$, 1.1 for $R=2$ and 0.5 for $R=3$.

The $Ti(O\text{-}iPr)_4$ solutions were aged for gelation at 30°C in a silicon-oil bath and set in a polyethylene container whose lid has one percent of the surface area exposing to the air. The gelation time t_g is defined as the reaction time at which no more fluidity is observed by tilting the solution container. All the prepared solutions could keep homogeneity throughout the gelation. The solutions with $R=1$ and 2 were transparent throughout the gelation, while the solution with $R=3$ became turbid, in spite of very slow water-supply rate.

SAXS measurements were performed at room temperature using an apparatus with a point focus Cu-Ka beam. Monochromatized X-ray incident beam was collimated by two collimators of aperture 0.5 mm × 0.5 mm. Scattered X-ray intensity was detected by a one-dimensional position-sensitive proportional counter. Most parts of the apparatus were loaded on a pair of rails whose positional deviation is less than 10 μm/100 mm. The detailed performance of the SAXS spectrometer used in this work has been described in a paper.[6] The count rate was corrected only for background scattering from pure EtOH in the same cell. The scattered intensity was determined as a function of the amplitude of the scattering vector, $h = 4\pi \sin\vartheta/\lambda$, where λ is the radiation wavelength and 2ϑ the scattering angle.

In the SAXS measurement, the scattered intensity from the ethanol component contained in the titanium alkoxide solution is never negligibly weak, especially in the h region beyond about 0.4 $Å^{-1}$. To observe the scattered intensity of the aggregation of titanium alkoxides only; the SAXS measurement was carried out for the samples of titanium solutions diluted to 10 : 1 with ethanol, and the scattered intensity of pure ethanol in a same cell was subtracted as a background from that of the titanium solutions in proportion to its transparency. Thus the scattered

intensites of the titanium solutions were determined.

3. RESULTS AND DISCUSSION

SAXS intensities for the $Ti(O\text{-}iPr)_4$ solutions in the molar ratios of $Ti : H_2O = 1 : R$ ($R=1$, 2 and 3) were measured at several reaction times in the gelation process. The SAXS intensities at the final stage of gelation are shown as a double-logarithmic plot in Fig. 1. The features of the SAXS intensities are summarized as follows: At low h values, all the scattered intensities have curvature, which will not be discussed in this paper. In the higher h region, log-log plots of the scattered intensities are well approximated by straight lines with different slopes depending on h regions. The slope in lower h region corresponds to power-law decay $\sim h^{-d_f}$ with $d_f=1.62\pm0.02$ for $R=1$, $d_f=1.74\pm0.01$ for $R=2$ and $d_f=2.51\pm0.04$ for $R=3$. In higher h region decays approximately follow the Porod law (i.e. $I(h)\sim h^{-4}$). The two lines with different slopes intersect at h values of about $0.5\,\text{Å}^{-1}$ for $R=1$, $0.3\,\text{Å}^{-1}$ for $R=2$ and $0.25\,\text{Å}^{-1}$ for $R=3$, respectively.

The scattered intensity begins to decay following the Porod law in the h region where h exceeds considerably the inverse of the size of the particle.[8] This demonstrates that TiO_2 solutions at the final stage of gelation are composed of aggregate of particles and have the fractal structure of fractal dimension d_f. Individual atoms never constitute the fractal structure. If

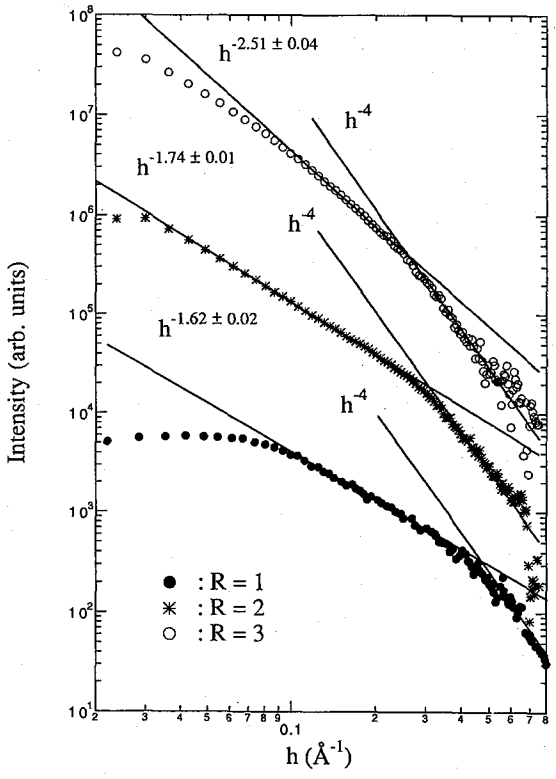

Fig. 1. SAXS intensities for $Ti(O\text{-}iPr)_4$ solutions of $R=1$, 2 and 3 at the final stage of gelation.

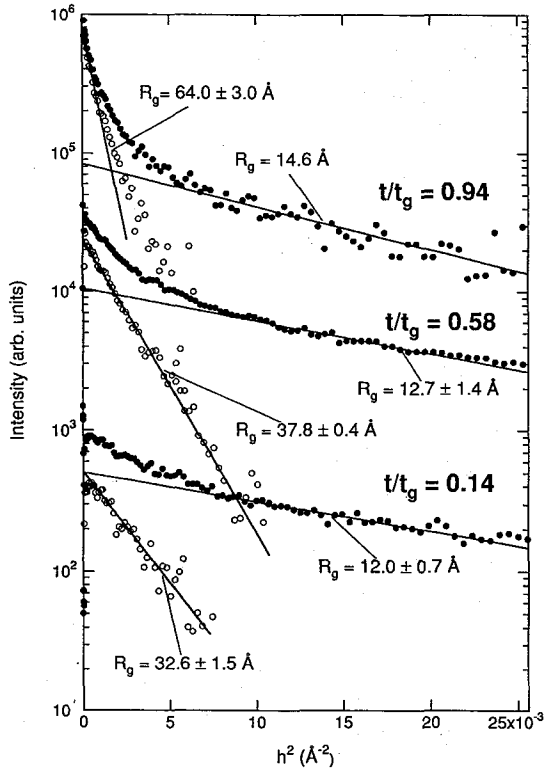

Fig. 2. Guinier plot of a Ti(O-iPr)$_4$ solution of R=2 at various lengths for annealing time. Open circles were obtained by subtracting the fitted straight line from measured scattered intensities (filled circles).

they do, the power-law decay would expand over the h region corresponding to atomic distances. The h values at the intersecting points may roughly give the size d of particles, $d \sim 13$ Å for R=1, ~ 21 Å for R=2 and ~ 25 Å for R=3 using the relation $d \sim 2p/h$.

The structural time-evolution of TiO_2 solutions is examined using the Guinier plot for the SAXS intensities measured at several reaction times in the gelation. The Guinier plot for molar ratio of R=2 is illustrated in Fig. 2. The scattered intensities (filled circles) can be well approximated by a straight line in the h regions beyond about 0.1 Å^{-1} throughout the gelation process. Open circles in Fig. 2 were obtained by subtracting the fitted straight line from the measured scattered intensities (the Fankuchen method). These open circles are also well approximated by straight lines (Fig. 2). The radii of gyration thus determined are plotted in Fig. 3.

Figure 3 demonstrates that TiO_2 solution consists of at least two different kinds of scatterers in size. The larger radii of gyration in Fig. 3 obtained from the curvatures in low h region as shown in Fig. 1 grow with rection time, and correspond to the size of fractal structures. The smaller radii of gyration correspond to the size of particles responsible for the Porod decay and almost hold constant throughout the gelation as shown in Fig. 3. These primary particles are formed just after the gelation process starts, and aggregate to form fractal structures. This is a gelation process of titanium iso-propoxide solutions.

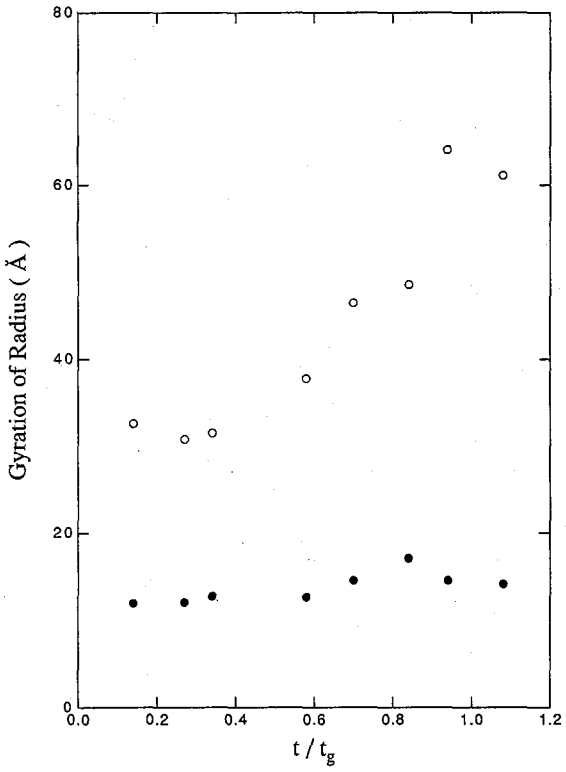

Fig. 3. The variation in the radius of gyration as a function of annealing time. Filled circles correspond to the size of primary particles and open circles correspond to that of fractal structures.

A similar behavior of the Guinier plot is also found for TiO_2 solutions with $R=1$ and 3. Measured values of the radius of gyration of primary particles are 5.0 ± 0.1 Å for $R=1$ and 11.0 Å for $R=3$. The Guinier plot for TiO_2 solutions of $R=1$ and 2 follows straight lines in the wide range of h as illustrated in Fig. 2. However, that for $R=3$ follows a straight line only in narrow h range and it is difficult to evaluate the radius of gyration with high accuracy.

There is a relationship between the SAXS results and the transparency or turbidity of TiO_2 solutions. The solution whose SAXS intensity shows the power-law decay in a wide h region keeps transparent throughout the gelation; while the solution whose SAXS intensity shows the power-law decay in a narrow h region becomes turbid before the gelation point. It is difficult to declare that the turbid TiO_2 solution of $R=3$ has a well-defined fractal structure.

4. COCLUSIONS

SAXS intensities at the final stage of sol-gel process of titnium iso-propoxide in acid condition show a characteristic feature of particle aggregation. Based on this SAXS study, we obtain the following conclusions.

Primary particles are formed just after the gelation process starts. The radii of gyration of primary particles vary as a function of R, that is 5.0 ± 0.1 Å for $R=1$, 12.0 ± 0.4 Å for $R=2$ and 11.0 Å for $R=3$, and almost hold constant throughout the gelation process.

The values of the radius of gyration are in rough agreement with the size of particles obtained using the relation $d \sim 2p/h$, where h is the boundary point between the fractal region and the Porod region. The relation $d \sim 2p/h$ gives the size ~ 13 Å for $R=1$, ~ 21 Å for $R=2$ and ~ 25 Å for $R=3$.

The primary particles aggregate to form fractal structures, whose fractal dimensions d_f are 1.62 ± 0.02 for $R=1$, 1.74 ± 0.01 for $R=2$ and 2.51 ± 0.04 for $R=3$. The size of the fractal structure increases with the reaction time.

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